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Direct determination of second-order density matrix using density equation: Open-shell system and excited state

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We formulated the density equation theory (DET) using the spin-dependent density matrix (SDM) as a basic variable and calculated the density matrices of the open-shell systems and excited states, as well as those of the closed-shell systems, *without* any use of the wave function. We calculated the open-shell systems, Be(^3S), Be^-(^2S), B^+(^3S), B(^2S), C^{2+}(^3S), C^+(^2S), N^{3+}(^3S), and N^{2+}(^2S), and the closed-shell systems, Be, Be^{2-}, B^+, B^-, C^{2+}, N^{3+}, H_2O, and HF. The new properties calculated are the transition energies and the spin densities at the nuclei. Generally speaking, the accuracy of the present results is slightly worse than that of the previous one using the spin-independent density matrix. © *2000 American Institute of Physics.* [S0021-9606(00)30320-8]

I. INTRODUCTION

Since all the operators appearing in quantum mechanics are one- and two-body ones, all elemental physical quantities can be determined from the second-order density matrices (2-DMs): The many-electron wave function involves more information than we need to know. Hence, it may be desirable to use the 2-DM as a basic variable of quantum mechanics instead of the wave function. However, a difficulty in this approach is that the *N*-representability condition, which is the condition enforced by the Pauli principle on the DMs, is still not completely known.

One of the authors proposed a nonvariational method for a direct determination of DM in time-independent[1] and time-dependent[2] cases. He showed that the density equation (DE) he derived is *equivalent* to the Schrödinger equation in the domain of *N*-representable DMs. However, the DE contains second-, third- and fourth-order DMs, so that the number of unknown variables exceeds the number of conditions. When the relations between these DMs are given by the *N*-representability condition,[2] or by some approximate concept, we can directly determine the DM by solving the DE. We call this approach the density equation theory (DET). A review of DET has been summarized recently.[3]

Valdemoro and co-workers[4] proposed approximate relations for 2-, 3-, and 4-DMs based on the fermion's anticommutation relation. We derived more accurate relations via Green's function method,[5,6] and successfully determined the 2-DMs of molecules for the first time without any use of the wave function. In terms of electron correlation, Valdemoro's formula correspond to the first-order approximations and ours to the second-order one. Mazziotti gave a reformulation of this approach and some refined approximation.[7,8] Recently, the DET has further been applied to the calculations of the potential energy curves, equilibrium geometries, and vibrational frequencies of molecules.[9] Here, we formulate the DET using spin-dependent DMs (SDMs) as basic variables, instead of the spin-independent ones, in order to apply it to open-shell and excited states.

II. THEORETICAL OUTLINE

The systems we are interested in are composed of *N* fermions, whose Hamiltonian involves up to two-body interaction terms,

$$\hat{H}=\sum_i v(i)+\sum_{i>j} w(i,j). \tag{2.1}$$

The matrix form of the Hamiltonian given by

$$H^{i_1 i_2}_{j_1 j_2}=w^{i_1 i_2}_{j_1 j_2}+\frac{1}{N-1}(v^{i_1}_{j_1}\delta^{i_2}_{j_2}+v^{i_1}_{j_2}\delta^{i_2}_{j_1}) \tag{2.2}$$

is convenient for the present study. Ensemble density matrix ρ is defined by

$$\rho=\sum_m \alpha_m \Psi_m \Psi^*_m, \tag{2.3}$$

where

$$0\leqslant\alpha_m\leqslant 1, \tag{2.4}$$

$$\sum_m \alpha_m=1, \tag{2.5}$$

and Ψ_m is an antisymmetric *N*-particle function. ρ describes a pure state when the sum consists of only a single term, i.e.,

$$\rho=\Psi\Psi^*. \tag{2.6}$$

The *n*th-order density matrices ${}^{(n)}\Gamma$ are defined by

$$ {}^{(n)}\Gamma(x'_1\cdots x'_n|x_1\cdots x_N)$$
$$ ={}_NC_n\int \rho(x'_1\cdots x'_n x_{n+1}\cdots x_N|x_1\cdots x_N)dx_{n+1}\cdots dx_N, \tag{2.7}$$

where x_i stands for the space-spin coordinate of *i*th electron and ${}_NC_n$ the binomial coefficient. Note that we do not integrate the spin variables of the first *n* particles, so that we are

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able to deal with *open-shell* system. We refer to ${}^{(2)}\Gamma$ as *n*-SDM or simply as *n*-DM. Second-quantized definition equivalent to Eq. (2.7) is

$$ {}^{(n)}\Gamma^{i_1 i_2 \cdots i_n}_{j_1 j_2 \cdots j_n} = \sum_m \frac{\alpha_m}{n!} \langle \Psi_m | a^\dagger_{i_1} a^\dagger_{i_2} \cdots a^\dagger_{i_n} a_{j_n} \cdots a_{j_2} a_{j_1} | \Psi_m \rangle, \tag{2.8} $$

where $a^\dagger$ and a denote creation and annihilation operators, respectively. The *n*-particle Green's function[10] is defined as

$$ G^{(n)}(x'_1 t'_1 \cdots x'_n t'_n | x_1 t_1 \cdots x_n t_n) = (-i)^n \langle T[\phi(x'_1 t'_1) \cdots \phi(x'_n t'_n) \phi(x_n t_n)^\dagger \cdots \phi(x_1 t_1)^\dagger)] \rangle, \tag{2.9} $$

where T denotes time-ordering operator and $\phi^\dagger$ and ϕ denote creation and annihilation field operators, respectively. The DMs are related to the Green's function by

$$ {}^{(n)}\Gamma(x'_1 \cdots x'_n | x_1 \cdots x_n) = \frac{(-i)^n}{n!} G^{(n)}(x'_1 0^- \cdots x'_n 0^- | x_1 0^+ \cdots x_n 0^+), \tag{2.10} $$

where 0^+ and 0^- denote positive and negative infinitesimals, respectively.

The *n*th-order density equation (DE)[1] is given by

$$ E^{(n)}\Gamma = \left\{ \sum_i^n v(i) + \sum_{i>j}^n w(i,j) \right\} {}^{(n)}\Gamma + (n+1) \times \int \left\{ v(n+1) + \sum_i^n w(i,n+1) \right\} {}^{(n+1)}\Gamma \, dx_{n+1} + \frac{1}{2}(n+1)(n+2) \int w(n+1,n+2) \times {}^{(n+2)}\Gamma \, dx_{n+1} \, dx_{n+2}. \tag{2.11} $$

In matrix form, it is given by

$$ E\langle \Psi | a^\dagger_{i_1} a^\dagger_{i_2} \cdots a^\dagger_{i_n} a_{j_n} \cdots a_{j_2} a_{j_1} | \Psi \rangle = \langle \Psi | \hat{H} a^\dagger_{i_1} a^\dagger_{i_2} \cdots a^\dagger_{i_n} a_{j_n} \cdots a_{j_2} a_{j_1} | \Psi \rangle. \tag{2.12} $$

The right hand side of these two equations are the *energy density matrix* (EDM), $R^{(n)}$ multiplied by ${}_N C_n$. One of the authors proved in 1976 that *each* DE with *n* larger than or equal to 2 is equivalent, in necessary and sufficient sense, to the Schrödinger equation if the density matrices involved are *N*-representable. The matrix form of the second-order DE is written as

$$ E\Gamma^{i_1 i_2}_{j_1 j_2} = \sum_{j_3 j_4 i_3 i_4} H^{i_3 i_4}_{j_3 j_4} \langle \Psi | a^\dagger_{i_1} a^\dagger_{i_2} a_{j_2} a_{j_1} a^\dagger_{i_3} a^\dagger_{i_4} a_{j_4} a_{j_3} | \Psi \rangle = \sum_{j_3 j_4} H^{j_1 j_2}_{j_3 j_4} \Gamma^{j_3 j_4}_{i_1 i_2} + 3 \sum_{j_3 j_4 i_4} H^{j_2 i_4}_{j_3 j_4} \Gamma^{j_1 j_3 j_4}_{i_1 i_2 i_4} + 3 \sum_{j_3 j_4 i_3} H^{i_3 j_1}_{j_3 j_4} \Gamma^{j_2 j_3 j_4}_{i_1 i_2 i_3} + 6 \sum_{j_3 j_4 i_3 i_4} H^{i_3 i_4}_{j_3 j_4} \Gamma^{j_1 j_2 j_3 j_4}_{i_1 i_2 i_3 i_4}. \tag{2.13} $$

Our purpose in this paper is to solve this DE. For this purpose, we have to represent approximately the 3,4-DMs included in the EDM in terms of the 1,2-DMs. We use the Green's function method for this purpose in the same way as in the previous paper,[5,6] but here the DMs explicitly involve the spin variables. The resultant decoupling formula of the 3,4-DMs are written using the wedge product form[7] as

$$ \begin{aligned} {}^{(3)}\Gamma = {}^{(1)}\Gamma^3 + 3({}^{(2)}\Gamma - {}^{(1)}\Gamma^2) \wedge {}^{(1)}\Gamma - \sum_k P_k (& U^{ki_1}_{j_1 j_2} U^{i_2 i_3}_{kj_3} + U^{ki_2}_{j_1 j_2} U^{i_3 i_1}_{kj_3} + U^{ki_3}_{j_1 j_2} U^{i_1 i_2}_{kj_3} + U^{j_1 j_2}_{ki_1} U^{kj_3}_{i_2 i_3} + U^{j_1 j_2}_{ki_2} U^{kj_3}_{i_3 i_1} \\ & + U^{j_1 j_2}_{ki_3} U^{kj_3}_{i_1 i_2} + U^{ki_2}_{j_2 j_3} U^{i_3 i_1}_{kj_1} + U^{ki_3}_{j_2 j_3} U^{i_1 i_2}_{kj_1} + U^{ki_1}_{j_2 j_3} U^{i_2 i_3}_{kj_1} + U^{j_2 j_3}_{ki_2} U^{kj_1}_{i_3 i_1} + U^{j_2 j_3}_{ki_3} U^{kj_1}_{i_1 i_2} + U^{j_2 j_3}_{ki_1} U^{kj_1}_{i_2 i_3} + U^{ki_3}_{j_3 j_1} U^{i_1 i_2}_{kj_2} \\ & + U^{ki_1}_{j_3 j_1} U^{i_2 i_3}_{kj_2} + U^{ki_2}_{j_3 j_1} U^{i_3 i_1}_{kj_2} + U^{j_3 j_1}_{ki_3} U^{kj_2}_{i_1 i_2} + U^{j_3 j_1}_{ki_1} U^{kj_2}_{i_2 i_3} + U^{j_3 j_1}_{ki_2} U^{kj_2}_{i_3 i_1}), \end{aligned} \tag{2.14} $$

$$ {}^{(4)}\Gamma = {}^{(1)}\Gamma^4 + 4({}^{(3)}\Gamma - {}^{(1)}\Gamma^3) \wedge {}^{(1)}\Gamma - 6({}^{(2)}\Gamma - {}^{(1)}\Gamma^2) \wedge {}^{(1)}\Gamma^2 + \tfrac{3}{4} U \wedge U, \tag{2.15} $$

where

$$ \Gamma^n = \underbrace{\Gamma \wedge \Gamma \cdots \wedge \Gamma}_{n \text{ times}}. \tag{2.16} $$

U is called collision term and defined by

$$ U = 2^{(2)}\Gamma - 2({}^{(1)}\Gamma \wedge {}^{(1)}\Gamma). \tag{2.17} $$

P_k is zero or unity for k being unoccupied and occupied, respectively. This decoupling approximation is essentially of the second-order in the correlation-correction perturbation. Note that for the 3-DMs, the UV term is not simply written down with the wedge product form and this is *not* an exact second-order correction, and we examined previously some correction terms.[6]

III. CALCULATIONAL METHOD

Our basic variable is the spin-dependent 2-SDM, which has about 16 times larger freedom than the spin-independent

TABLE I. Results for the triplet states: total energy (in a.u.), correlation energy error (in %), and rms deviation of the $^{(2)}\Gamma$ calculated by the DET and the wave function method. Active space denotes number of occupied MOs×virtual MOs and electrons denotes number of α electrons+β electrons, respectively.

System	Active space electrons	State	Total energy (correlation energy error in %) $^{(2)}\Gamma$ error[a] DET	HF	SDCI	FCI
Be	4×4	^3S	−13.314 66 (−0.2)	−13.303 61 (100)	−13.314 64 (0.0)	−13.314 64
	3+1		1.43×10^{-3}	2.67×10^{-2}	0	0
B^+	4×4	^3S	−23.605 34 (−0.2)	−23.592 33 (100)	−23.605 32 (0.0)	−23.605 32
	3+1		5.21×10^{-3}	2.66×10^{-2}	0	0
C^{2+}	4×4	^3S	−35.304 35 (−0.3)	−35.291 53 (100)	−35.304 31 (0.0)	−35.304 31
	3+1		6.10×10^{-3}	2.14×10^{-2}	0	0
N^{3+}	4×4	^3S	−49.362 84 (−0.2)	−49.348 52 (100)	−49.362 81 (0.0)	−49.362 81
	3+1		4.54×10^{-3}	2.32×10^{-2}	0	0

[a]Square norm of the difference between the calculated 2-SDM and FCI one.

2-DM. It is hermitian and antisymmetric. The 3,4-SDMs are represented in terms of the 1,2-SDMs by Eqs. (2.14) and (2.15). The solution of the DE corresponds to finding the vanishing value of the function, $\boldsymbol{f}$,

$$\boldsymbol{f}(^{(2)}\Gamma) = {}_N C_2 R(^{(2)}\Gamma) - E^{(2)}\Gamma. \tag{3.1}$$

This function is linearized and solved by using the Newton–Raphson method. The algorithm is essentially the same as the previous one[5,6] and is summarized as follows:

(1) Guess initial 2-SDM, which is ordinally Hartree–Fock (HF) $^{(2)}\Gamma$.
(2) Calculate $E=\mathrm{Tr}(^{(2)}\Gamma H)$.
(3) Construct 3,4-SDM $^{(3)}\Gamma$ and $^{(4)}\Gamma$ with $^{(2)}\Gamma$ and $^{(1)}\Gamma$ by Eqs. (2.14) and (2.15).
(4) Calculate the error function $\boldsymbol{f}$ by Eq. (3.1).
(5) Update 2-SDM using the Newton–Raphson method.
(6) Repeat procedures (2)–(5) until convergence.
(7) Check the N-representability of the resultant $^{(2)}\Gamma$.

In applying the Newton–Raphson method,[11] we need to calculate the coefficient matrix $A_{ij}=\partial f_i/\partial x_j$, where x denote the variable $^{(2)}\Gamma$ itself and i,j denote the four indices of $^{(2)}\Gamma$.

As an initial guess of the 2-SDM, we used the HF estimate,

$$^{(2)}\Gamma^{i_1 i_2}_{j_1 j_2} = \tfrac{1}{2}(\delta^{i_1}_{j_1}\delta^{i_2}_{j_2} - \delta^{i_1}_{j_2}\delta^{i_2}_{j_1}), \tag{3.2}$$

where δ^i_j is Kronecker's delta, but when the convergency was not good, we used even the full CI(FCI) 2-SDM.

The above procedure was applied to the open-shell atoms, Be(^3S), Be^-(^2S), B^+(^3S), B(^2S), C^{2+}(^3S), C^+(^2S), N^{3+}(^3S), N^{2+}(^2S) and the closed-shell atoms and molecules, Be, Be^{2-}, B^+, B^-, C^{2+}, N^{3+}, H_2O and HF. The basis set of Be is double-ζ s-type STO[12] expanded by six GTOs.[13] For B, C and N, double-ζ s-type GTOs by Huzinaga[14] and Dunning[15] were used. For H_2O and HF, STO-6G basis was used. The geometries of H_2O and HF are the experimental ones.[16]

TABLE II. Results for the doublet states: total energy (in a.u.), correlation energy error (in %), and rms deviation of the $^{(2)}\Gamma$ calculated by the DET and the wave function method. Active space denotes number of occupied MOs×virtual MOs and electrons denotes number of α electrons+β electrons, respectively.

System	Active space electrons	State	Total energy (correlation energy error in %) $^{(2)}\Gamma$ error[a] DET	HF	SDCI	FCI
Be^-	5×3	^2S	−13.240 20 (−)	⋯	⋯	−13.240 16
	3+2		2.20×10^{-3}	⋯	⋯	0
B	5×3	^2S	−24.114 36 (−0.3)	−24.097 47 (100)	−24.114 31 (0.0)	−24.114 31
	3+2		6.03×10^{-3}	2.28×10^{-1}	3.55×10^{-5}	0
C^+	5×3	^2S	−36.556 58 (−0.2)	−36.542 03 (100)	−36.556 55 (0.0)	−36.556 55
	3+2		3.77×10^{-3}	1.24×10^{-1}	1.56×10^{-5}	0
N^{2+}	5×3	^2S	−51.614 76 (−0.2)	−51.602 38 (100)	−51.614 74 (0.0)	−51.614 74
	3+2		2.47×10^{-3}	1.73×10^{-2}	7.71×10^{-6}	0

[a]Square norm of the difference between the calculated 2-SDM and FCI one.

TABLE III. Results for the closed-shell atoms and molecules: total energy (in a.u.), correlation energy error (in %), and rms deviation of the $^{(2)}\Gamma$ calculated by the DET and the wave function method. Active space denotes number of occupied MOs×virtual MOs and electrons denotes number of α electrons+β electrons, respectively.

System	Active space electrons	State	Total energy (correlation energy error in %) $^{(2)}\Gamma$ error[a] DET	HF	SDCI	FCI
Be	4×4	^1S	−14.582 70 (−0.1)	−14.568 53 (100)	−14.582 69 (0.0)	−14.582 69
	2+2		4.25×10^{-5}	4.58×10^{-2}	1.06×10^{-4}	0
Be^{2-}	6×2	^1S	−11.268 39 (0.0)	−11.258 96 (100)	−11.268 39 (0.0)	−11.268 39
	3+3		1.32×10^{-5}	2.00×10^{-2}	0	0
B^+	4×4	^1S	−24.249 08 (1.5)	−24.234 34 (100)	−24.249 29 (0.1)	−24.249 31
	2+2		5.19×10^{-5}	6.03×10^{-2}	5.17×10^{-4}	0
B^-	6×2	^1S	−23.669 08 (−0.2)	−23.656 64 (100)	−23.669 05 (0.0)	−23.669 05
	2+2		5.83×10^{-6}	2.46×10^{-2}	0	0
C^{2+}	4×4	^1S	−36.417 74 (0.1)	−36.403 82 (100)	−36.417 75 (0.1)	−36.417 76
	2+2		1.47×10^{-4}	3.92×10^{-2}	1.84×10^{-4}	0
N^{3+}	4×4	^1S	−51.087 62 (−0.1)	−51.074 23 (100)	−51.087 60 (0.1)	−51.087 61
	2+2		7.39×10^{-5}	8.25×10^{-2}	7.96×10^{-5}	0
H_2O	8×4	$^1A_1$	−75.725 50 (6.9)	−75.678 85 (100)	−75.728 21 (1.5)	−75.728 94
	4+4		9.22×10^{-3}	2.59×10^{-1}	7.83×10^{-3}	0
HF	8×2	$^1\Sigma$	−99.523 61 (8.4)	−99.499 84 (100)	−99.525 77 (0.0)	−99.525 77
	4+4		1.32×10^{-5}	2.00×10^{-2}	0	0

[a]Square norm of the difference between the calculated 2-SDM and FCI one.

IV. RESULTS

First, we examine the energy and $^{(2)}\Gamma$ calculated by the present DET. Tables I, II and III show the total energy, the correlation energy error, and the root mean square deviation of the SDMs calculated by the present DET for the open-shell triplet, doublet, and the closed-shell singlet states, respectively. Since only *s*-type basis sets are used for atoms, doublet states of the five-electron atoms are not the ground ^2P state but actually the excited ^2S states and the triplet states of the four-electron atoms are also not the ^3P state but the ^3S state. Computationally, such *S* states are easier to calculate than the *P* states. For the triplet states summarized in Table I, the errors in the correlation energy are less than 0.3% and the total energies of the DET slightly overshoot those of the FCI. Since the DET is not variational, this overshooting happened, though it is small. The rms (root-mean-square) deviation of the SDM is in the order of 10^{-3}, and is much smaller than the HF ones. For the doublet states shown in Table II, the DET also reproduces well the FCI results almost in the same accuracy as those of the triplet states. For the closed-shell singlet states given in Table III, the energy and $^{(2)}\Gamma$ of the DET show much better agreement with the FCI ones in comparison with the triplet and doublet states. It

TABLE IV. Transition energy, ionization energy and electron affinity (in a.u.) calculated by the DET and the wave function method.

System	Transition	DET	HF	SDCI	FCI
Be	$^1S\rightarrow{}^3S$	1.268 04	1.264 92	1.268 05	1.268 05
	$^1S+e^-\rightarrow{}^2S$	1.342 49	⋯	⋯	1.342 53
B	$^2S+e^-\rightarrow{}^1S$	0.445 28	0.440 83	0.445 26	0.445 26
	$^2S-e^-\rightarrow{}^1S$	−0.134 72	−0.136 87	−0.134 98	−0.135 00
B^+	$^1S\rightarrow{}^3S$	0.643 74	0.642 01	0.643 97	0.643 99
C^{2+}	$^1S\rightarrow{}^3S$	1.113 39	1.112 29	1.113 44	1.113 45
	$^1S+e^-\rightarrow{}^2S$	−0.138 84	−0.138 21	−0.138 80	−0.138 79
N^{3+}	$^1S\rightarrow{}^3S$	1.724 78	1.725 71	1.724 79	1.724 80
	$^1S+e^-\rightarrow{}^2S$	−0.527 14	−0.528 15	−0.527 14	−0.527 13

TABLE V. $\langle N_\alpha\rangle$, $\langle N_\beta\rangle$, $\langle S_z\rangle$ and $\langle S^2\rangle$ calculated for the 2-SDM by the DET.

System	State	$\langle N_\alpha\rangle$	$\langle N_\beta\rangle$	$\langle S_z\rangle$	$\langle S^2\rangle$
Be	^3S	3.000 72	0.999 28	1.000 72	2.000 03
B^+	^3S	2.997 41	1.002 59	0.997 41	2.002 37
C^{2+}	^3S	3.003 05	0.996 94	1.003 06	2.000 06
N^{3+}	^3S	3.002 20	0.997 80	1.002 20	2.000 05
Be^-	^2S	2.999 22	2.000 78	0.499 22	0.750 01
B	^2S	3.001 61	1.998 39	0.501 61	0.750 00
C^+	^2S	3.001 13	1.998 87	0.501 13	0.750 00
Be	^1S	2.000 00	2.000 00	0.000 00	8.90×10^{-6}
Be^{2-}	^1S	3.000 00	3.000 00	0.000 00	4.63×10^{-7}
B^+	^1S	2.000 04	2.000 04	0.000 00	4.13×10^{-4}
B^-	^1S	3.000 00	3.000 00	0.000 00	-1.94×10^{-6}
C^{2+}	^1S	2.000 00	2.000 00	0.000 00	3.87×10^{-5}
N^{3+}	^1S	2.000 00	2.000 00	0.000 00	4.74×10^{-6}
H_2O	$^1A_1$	5.000 02	5.000 02	0.000 00	1.28×10^{-2}
HF	$^1\Sigma$	5.000 02	5.000 02	0.000 00	1.03×10^{-2}

TABLE VI. Minimum eigenvalues of the P, Q and G matrices, numbers of the eigenvalues smaller than -1.0×10^{-6} in the parentheses, and the range of eigenvalues of 1-SDM calculated by the DET.

System	Active electrons	P-matrix	Q-matrix	G-matrix	1-SDM
Be(^3S)	4	$-6.545\times10^{-4}(7)$	$-6.688\times10^{-4}(7)$	$-7.047\times10^{-4}(17)$	$-3.536\times10^{-4}\sim1.0004$
B^+(^3S)	4	$-1.815\times10^{-4}(4)$	$-1.896\times10^{-4}(3)$	$-1.937\times10^{-4}(11)$	$3.067\times10^{-4}\sim0.9997$
C^{2+}(^3S)	4	$-3.009\times10^{-3}(8)$	$-3.015\times10^{-3}(9)$	$-3.132\times10^{-3}(24)$	$-1.548\times10^{-3}\sim1.0016$
N^{3+}(^3S)	4	$-2.237\times10^{-3}(7)$	$-2.242\times10^{-3}(7)$	$-2.235\times10^{-5}(23)$	$1.154\times10^{-3}\sim1.0012$
Be^-(^2S)	5	$-4.952\times10^{-6}(1)$	$-6.809\times10^{-6}(8)$	$-7.965\times10^{-6}(6)$	$2.659\times10^{-4}\sim1.0000$
B(^2S)	5	$-2.123\times10^{-3}(6)$	$-2.121\times10^{-4}(10)$	$-4.233\times10^{-4}(23)$	$-2.102\times10^{-4}\sim1.0021$
C^+(^2S)	5	$-1.331\times10^{-3}(5)$	$-3.015\times10^{-3}(7)$	$-3.132\times10^{-3}(18)$	$-1.316\times10^{-3}\sim1.0000$
N^{2+}(^2S)	5	$-1.555\times10^{-5}(2)$	$-1.396\times10^{-4}(10)$	$-2.928\times10^{-4}(14)$	$-1.154\times10^{-3}\sim1.0012$
Be(^1S)	4	$-6.246\times10^{-6}(1)$	$-3.938\times10^{-6}(2)$	$-4.781\times10^{-6}(4)$	$1.119\times10^{-4}\sim0.9997$
Be^{2-}(^1S)	6	ok	$-3.045\times10^{-6}(5)$	$-4.576\times10^{-6}(6)$	$1.996\times10^{-4}\sim1.0000$
B^+(^1S)	4	$-6.963\times10^{-6}(4)$	$-1.563\times10^{-5}(5)$	$-4.576\times10^{-6}(12)$	$1.996\times10^{-4}\sim1.0000$
B^-(^1S)	6	ok	$-1.417\times10^{-4}(4)$	$-1.986\times10^{-4}(6)$	$3.009\times10^{-4}\sim1.0000$
C^{2+}(^1S)	4	$-3.818\times10^{-5}(5)$	$-2.019\times10^{-6}(1)$	$-1.998\times10^{-5}(7)$	$5.863\times10^{-4}\sim0.9998$
N^{3+}(^1S)	4	$-1.922\times10^{-5}(2)$	ok	$-1.111\times10^{-5}(7)$	$1.168\times10^{-1}\sim0.9999$
H_2O($^1A_1$)	8	$-6.793\times10^{-4}(2)$	$-4.830\times10^{-4}(18)$	$-6.606\times10^{-4}(5)$	$1.427\times10^{-2}\sim0.9987$
HF($^1\Sigma$)	8	$-8.303\times10^{-4}(1)$	$-7.688\times10^{-4}(14)$	$-1.221\times10^{-3}(5)$	$1.696\times10^{-2}\sim0.9994$

should be noted that the $^{(2)}\Gamma$ by the DET is more accurate than those of the SDCI, since the DET determines the DM directly.

The transition energy, ionization energy, and electron affinity are summarized in Table IV for Be, B, C, and N atoms. These quantities are calculated for the first time by the DET. Since some states involved are not the normal ground and excited states, the values themselves may look strange, but the DET results are very close to the FCI ones. The deviations of the DET values from the FCI ones are less than 2.8×10^{-4} a.u., while those of the HF and SDCI methods are 4.42×10^{-3} and 2×10^{-5}, respectively.

The expectation values of the numbers of α and β spin electrons, $\langle N_\alpha\rangle$ and $\langle N_\beta\rangle$, and those of the operators S_z and S^2, $\langle S_z\rangle$ and $\langle S^2\rangle$, are calculated and summarized in Table V for the triplet, doublet, and singlet states. For the closed-shell singlet state, we obtain almost correct expectation values for atoms, but the deviations are somewhat large for molecules, especially for $\langle S^2\rangle$. For the open-shell triplet and doublet states, the expectation values $\langle N_\alpha\rangle$, $\langle N_\beta\rangle$, $\langle S_z\rangle$ and $\langle S^2\rangle$ slightly deviate from the exact values. This is because the present approximate decoupling technique does not include any restrictive conditions for the numbers of the electrons and spins. When we enforce the ''normalization'' condition, the calculations were not improved and even did not converge.

Next, we examine the N-representability conditions for the 1-SDM and 2-SDM. Table VI gives the occupation numbers of the natural orbitals of the 1-SDM, and the lowest eigen values of the P, Q and G matrices.[17] For the closed-shell systems, the N-representability condition of the 1-SDM is completely satisfied, i.e., the occupation numbers are all positive and less than unity. This was also so in the previous spin-free calculations.[5,6] However, the violation of the N-representability of the 1-SDM occurs for some open-shell atoms. The P, Q and G are necessary conditions for the N-representability of the 2-SDM: The eigenvalues of the P, Q and G matrices should be nonnegative. However, some of the eigenvalues are slightly negative, though the violations seem to be small. The extent of the violation seems to increase as the number of the electrons increases, and seems to be larger for the open-shell systems than for the closed-shell systems.

Table VII shows the second moment of electron distribution, $\langle r^2\rangle$. Again, the DET results for the closed-shell systems are better than those for the open-shell systems. Some of them are better than the SDCI results, because the DET directly determines the SDM. For the open-shell systems, the SDCI results are superior to the DET ones, because the violation of the N-representability condition tends to accumulate electrons near the nucleus. Some of the SDCI results are identical to the FCI one: as for the active space, it is small, the single and double excitations span the complete space.

Finally, the spin density and the electron density at the nucleus are calculated. In Tables VIII, IX and X, the results are shown for the triplet, doublet, and singlet states, respec-

TABLE VII. Second moment ($\langle r^2\rangle$) of atoms calculated by the DET and the wave function method.

System	State	DET	HF	SDCI	FCI
Be	^3S	−4.850 06	−4.850 21	−4.850 06	−4.850 06
B^+	^3S	−4.950 63	−4.950 74	−4.950 70	−4.950 70
C^{2+}	^3S	−3.274 01	−3.274 04	−3.274 02	−3.274 02
N^{3+}	^3S	−2.339 06	−2.339 08	−2.339 06	−2.339 06
Be^-	^2S	−7.331 25	⋯	⋯	−7.331 28
B	^2S	−6.458 84	−6.457 65	−6.458 89	−6.458 92
C^+	^2S	−4.081 58	−4.081 19	−4.081 59	−4.081 60
N^{2+}	^2S	−2.849 06	−2.848 92	−2.849 07	−2.849 07
Be	^1S	−5.771 25	−5.777 82	−5.771 36	−5.771 27
Be^{2-}	^1S	−9.563 53	−9.563 89	−9.563 55	−9.563 55
B^+	^1S	−2.719 24	−2.698 94	−2.718 49	−2.718 87
B^-	^1S	−9.812 36	−9.812 53	−9.812 37	−9.812 37
C^{2+}	^1S	−1.561 49	−1.555 44	−1.561 44	−1.561 52
N^{3+}	^1S	−1.021 44	−1.019 32	−1.021 43	−1.021 45

TABLE VIII. Electron density and spin density at the nucleus of the triplet state. ρ denotes the total electron density, and ρ_α and ρ_β are the α and β electron densities, respectively, and $\Delta\rho=\rho_\alpha-\rho_\beta$ is spin density at the nucleus.

System (state)	DET	HF	SDCI	FCI
Be(^3S)				
ρ	32.530	32.401	32.530	32.530
ρ_α	18.069	17.593	18.068	18.068
ρ_β	14.461	14.808	14.462	14.462
$\Delta\rho$	3.608	2.785	3.605	3.605
$B^+(^3S)$				
ρ	68.741	68.680	68.742	68.742
ρ_α	36.216	35.947	36.225	36.225
ρ_β	32.525	32.733	32.517	32.517
$\Delta\rho$	3.691	3.215	3.708	3.708
$C^{2+}(^3S)$				
ρ	122.143	122.064	122.143	122.143
ρ_α	64.502	64.083	64.489	64.489
ρ_β	57.641	57.981	57.654	57.654
$\Delta\rho$	6.860	6.103	6.836	6.836
$N^{3+}(^3S)$				
ρ	197.798	197.705	197.798	197.798
ρ_α	104.557	103.989	104.543	104.543
ρ_β	93.241	93.716	93.255	93.255
$\Delta\rho$	11.316	10.273	11.287	11.287

tively. The spin density at the nucleus is a very important observable in ESR and other magnetic chemistry and calculated for the first time by the DET. The DET well reproduces the spin density at the nucleus of the FCI method. The results are almost in the same accuracy as the SDCI ones and much better than the HF ones, since the DET includes both electron and spin correlations up to second-order in the perturbation. The spin densities calculated within the HF method do not include the spin polarization effects[18,19] and therefore

TABLE IX. Electron density and spin density at the nucleus of the doublet state. ρ is the total electron density, and ρ_α and ρ_β are the α and β electron densities, respectively, and $\Delta\rho=\rho_\alpha-\rho_\beta$ is the spin density at the nucleus.

System (state)	DET	HF	SDCI	FCI
$Be^-(^2S)$				
ρ	33.568	⋯	⋯	33.568
ρ_α	17.909	⋯	⋯	17.911
ρ_β	15.659	⋯	⋯	15.658
$\Delta\rho$	2.249	⋯	⋯	2.253
B(^2S)				
ρ	70.058	69.998	70.058	70.058
ρ_α	35.980	35.796	35.977	35.977
ρ_β	34.078	34.202	34.081	34.081
$\Delta\rho$	1.902	1.594	1.896	1.896
$C^+(^2S)$				
ρ	125.313	125.238	125.313	125.313
ρ_α	64.033	63.809	64.030	64.030
ρ_β	61.280	61.429	61.284	61.283
$\Delta\rho$	2.753	2.380	2.746	2.746
$N^{2+}(^2S)$				
ρ	203.820	203.732	203.820	203.820
ρ_α	103.832	103.564	103.828	103.828
ρ_β	99.989	100.168	99.992	99.992
$\Delta\rho$	3.843	3.396	3.836	3.836

TABLE X. Electron density at the nucleus of the singlet state.

System (state)	DET	HF	SDCI	FCI
Be(^1S)	31.489	31.352	31.489	31.489
$Be^{2-}(^1S)$	34.316	34.209	34.316	34.316
$B^+(^1S)$	69.030	68.983	69.031	69.031
$B^-(^1S)$	71.456	71.399	71.457	71.457
$C^{2+}(^1S)$	123.532	123.470	123.532	123.532
$N^{3+}(^1S)$	201.055	200.978	201.055	201.055

are always smaller than the DET and FCI values. For the closed-shell singlet states, the spin density is exactly zero, therefore, only the total density of the electrons at nucleus is given. The accuracy of the DET is almost the same as that of SDCI.

V. CONCLUSION

We successfully calculated the SDMs of some open-shell and excited states for the first time by the spin-explicit DET without *any use* of the wave function. The same method is also applied to the closed-shell systems, though the solution is easier with the spin-free formalism. Generally speaking, the quality of solutions were better for the closed-shell systems than for the open-shell systems. A reason is a larger number of variables to be solved for open-shell systems. As seen from the results, the present method and the solution algorithm are not yet complete and needs some future refinement. Nonetheless, the present results constitutes a milestone in the DET approach in theoretical chemistry as its first application to open-shell and excited states.

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